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PREPARATION AND PROPERTIES OF STYRENATED ALLYL STARCH

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Preparation of allyl starch³ and its potentialities as a raw material for coatings were announced in 1945 (15). Since that time, this material, a soluble, unsaturated polymeric starch derivative capable of oxidative polymerization to coatings unusually resistant to organic solvents and heat, has received attention from several laboratories and industrial concerns. A number of other publications have also appeared. Dietz, Hansen and Gallagher (5) have recommended some formulations suitable for indoor coatings. Other publications were concerned with methods of making allyl starch (3, 8, 12, 13, 16, 21) compatibility with resins (5), commercial applications (7), mixed ethers (9, 10, 22), polymerization of allyl ethers by heat and oxygen (18, 23), and formulations for specific purposes (14, 17). A similar but low molecular weight ether from sucrose has been developed (19, 24). It has been shown (22) that films of benzyl ether of allyl starch have greater water resistance than films of unmodified allyl starch.

The present paper describes the preparation of allyl starch-styrene copolymers and gives the properties of coatings made from them. The baked styrenated allyl starch coatings retain the excellent solvent resistance of allyl starch and, in addition, have good resistance to both cold and hot water. Because of the improved properties of the copolymers, ease of preparation, and the low cost of styrene, it is believed that styrenated allyl starch is a raw material of considerable promise.

Styrenation of Allyl Starch

In view of the high molecular weight of allyl starch and the likelihood of premature gelation, copolymerization in solution (2, 11) rather than in mass (4, 20) appeared to be desirable. To counteract the cross-linking tendency of the allyl starch during copolymerization and to secure homogeneity by reducing the length of the polystyrene chains formed, several polymerization modifiers, or regulators, were tried. Commercial dipentene, previously employed as a regulatory solvent in the solution styrenation of drying oils (2), proved satisfactory in the present investigation. Allyl starch was used as an approximately 40% solution in toluene (containing some butanol to reduce viscosity), and the styrene was used as a solution of identical concentration in dipentene.

An investigation of the effect of the ratio of allyl starch to styrene demonstrated that good results are obtained when these two reactants are

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³ THE ALLYL STARCH DISCUSSED IN THIS PAPER HAS APPROXIMATELY 1.8 ALLYL GROUPS AND 1.2 HYDROXYL GROUPS PER GLUCOSE UNIT. THIS MATERIAL IS COMMERCIALY AVAILABLE (7).

present in equivalent amounts, calculated on a double-bond basis. Allyl starch of 1.8 substitution has a formula weight of 234, so that 130 grams corresponds to 1 allyl double bond. Similarly 104 grams of styrene corresponds to 1 vinyl double bond.

The reaction mixture is stirred at 100° C in the presence of a catalyst (such as cumene hydroperoxide) until the viscosity (measured at 25° C.) is 3 stokes or more, when 80 to 85% of the styrene should be converted to polymeric material. The time required to obtain this degree of conversion ranges as a rule from about 12 to 24 hours, although in some cases longer reaction periods are required.

In a specific preparation the quantities used were:

Experiment No. 62-1

	Grams
Allyl Starch	117
Toluene butanol	186
Styrene	94
Dipentene	149
Cumene hydroperoxide	5.67

To provide the allyl starch, 302 grams of a 38.6% solution of allyl starch in toluene butanol (95-5) was used. A styrene solution of identical concentration was made by mixing 94 grams of styrene with 149 grams of commercial dipentene. The cumene hydroperoxide (7.27 grams of a solution assaying⁴ 78%) was added to the styrene-dipentene solution. Both main solutions were then transferred to the reaction vessel, a liter flask fitted with glass half-moon stirrer and reflux condenser. The flask was set in a bath automatically maintained at 100° C. The reaction mixture was mechanically stirred at this temperature until the appropriate conversion was obtained. To follow the course of the reaction, viscosity at 25° C. was determined on samples periodically removed from the reaction mixture. After 14 hours, when the viscosity was 3 stokes, the heating was discontinued. The reaction mixture then had 36.2% nonvolatile material (as determined by heating a 2-gram sample to constant weight at 135° C in the presence of 0.2% hydroquinone to inhibit further polymerization). This indicated an 83% conversion of the styrene.

Properties of Styrenated Allyl Starch

Styrenated allyl starch freed of solvent is a thermoplastic solid of moderate hardness. It is soluble in aromatic solvents, such as toluene, that contain small amounts of polar solvent like ethanol or butanol. Such solutions of styrenated allyl starch tolerate much more dilution with saturated hydrocarbons than corresponding solutions of the original allyl starch.

⁴ BY A MODIFIED WHEELER METHOD (GARDNER & SWARD *Physical and Chemical Examination of Paints, Varnishes, Lacquers & Colors*, 10TH ED. P. 433 (1946). WHEELER. *Oil and Soap*, 9, 89 (1934). WITH CUMENE HYDROPEROXIDE. PEROXIDE VALUES FOUND ARE A FUNCTION OF TIME. A CONSTANT VALUE BEING OBTAINED ONLY WHEN A REACTION TIME OF 45 MINUTES OR LONGER IS USED.

Since plasticizers might be required for certain purposes, compatibility characteristics of styrenated allyl starch were studied. Chlorinated biphenyls, such as the Arochlors, had about the same high compatibility with both the styrenated and the unstyrenated product. Differences were noticed, however, with ester-type plasticizers. Paraplex G 5C, for instance, was more compatible with styrenated allyl starch, whereas Paraplex RC 7 was more compatible with untreated material.

Coatings from Styrenated Allyl Starch

When styrenated allyl starch was to be used as a lacquer, the solution obtained at the end of the reaction period was reduced with added solvent to the desired viscosity, which ranged from 1.5 stokes for brushing to about 0.5 stoke for spraying.

In the preparation described in detail, a small amount of toluene-butanol (95:5) reduced the viscosity to 1.5 stokes and lowered the percentage solids only slightly, to 35.9%.

Lacquers so obtained are promising as protective and decorative finishes for wood, metal, glass, and similar surfaces. The formulations so far studied have given best results as baked coatings.

Evaluation of Films

As a preliminary step in evaluation of lacquers in our practice, cure-times were first determined. Small glass plates were coated by pouring on the lacquer solution and allowing them to drain in a nearly vertical position.

For determination of the cure time of baked films, several coated panels were heated in a forced circulation oven controlled at 150° C. Panels were removed after 10, 20, 30, 40 and 60 minutes. The period that produced films resistant to scarring by the fingernail was taken as the cure time.

Oblong pieces of plate glass were then coated with uniform films of the lacquer (about 0.5 mil thick) by means of a doctor blade; the films were cured for the period indicated in the cure time tests, and hardness was determined by the method of Sward (6).

Films applied to steel panels and similarly cured were subjected to the standard ASTM elongation test (1).

Films were also applied to 5/8- x 6 inch test tubes with a mechanical dip-coater. The lacquer solution was held in a 27-mm. diameter graduate, from which the test tubes were withdrawn at the rate of 2 inches per minute. The coated tubes, inverted on a rack, were baked for the cure time previously determined. The cured films were tested by suspending the test tubes in the following: 50% aqueous ethanol, 4% acetic acid, 5% sodium hydroxide, acetone, soapy water⁵ and distilled water at room temperature and at 100° C.

⁵ ONE % SOLUTION OF COMMERCIAL SOAP POWDER.

The films were examined for damage according to the following schedule: Every 10 minutes for the first hour, hourly for 7 hours, then at 24, 48, and 72 hours. The time when failure (local or general disintegration of the film) was noted was reported. In general tests for resistance to solutions were discontinued after 72 hours; tests in boiling water were discontinued after 12 hours.

Results of Tests

Table I shows results obtained on styrenated allyl starch lacquer (No. 62-1), together with corresponding data for unmodified allyl starch and allyl starch specially compounded for water resistance (7).

The Sward Hardness value of 51 shown by styrenated allyl starch 62-1 was satisfactory, being only slightly lower than the figures for unstyrenated products. The elongation of styrenated allyl starch films was rather low; like that of unmodified allyl starch it can be improved by addition of plasticizer. The subject will be discussed in detail in a later publication.

In resistance to the various test solutions, marked improvement was evident. As compared with unmodified allyl starch coatings (Experiments 116-119, 116-1C, 116-5G, 116-7), the lacquer made from the styrenated material (Experiment 62-1) had in most cases substantially increased resistance to aqueous alcohol, soapy water, and distilled water both at room temperature and at 100° C. It was also superior to allyl starch films plasticized with Beckosol 1308 and Duraplex KD 75, respectively. Although the specially compounded allyl starch, VR (7) had excellent resistance to most aqueous solutions, the styrenated allyl starch was harder and had greater resistance to boiling water.

Summary

A simple procedure is described for solution copolymerization of allyl starch with styrene. Cumene hydroperoxide was used as initiator, and dipentene was employed as polymerization regulator.

Styrenated allyl starch so prepared has promise as a baking lacquer. As compared with unmodified allyl starch, it has substantially increased resistance to aqueous alcohol, soapy water, distilled water and boiling water.

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Table I

Evaluation of Allyl Starch and Styrenated Allyl Starch Coatings

Experiment No.	116-1	116-19 ^a	116-10 ^a	116-5G ^a	116-5 ^b	116-10A ^c	116-10B ^c	WR ^d
Styrenated allyl starch, parts	100	C	C	O	C	C	C	-
Allyl starch, parts	C	100	100	100	100	100	100	-
Beckosol 1308, parts	C	C	C	C	C	30	C	-
Duraplex 1175, parts	C	C	C	C	C	C	30	-
Cure time at 150° C., min.	30	20	30	30	30	20	30	90 ^e
Sward hardness	51	60	68	72	79	52	54	28
Elongation, %	4	5	4	4	7	>30	>30	>30
Resistance of baked films (hrs.) to:								
50% ethanol	>72	2	10 min.	0.5	2	3	4	>72
4% acetic acid	24	48	2	4	24	>72	48	24
5% sodium hydroxide	3	24	20 min.	C.5	C.75	1	24	>72
Acetone	C	1	2	2	8	2	2	>72
Soapy water	>72	>72	2	2	7	72	24	>72
Distilled water	>72	24	2	8	48	>72	>72	>72
Boiling water	>12	1 min.	1 min.	1 min.	1 min.	10 min.	1 min.	0.25

^a Made in this Laboratory from allyl starch solids kindly supplied by General Mills, Inc.

^b Made from allyl starch solids prepared in this Laboratory.

^c In experiments 116-10A and 116-10B, plasticizers were added to solution 116-10.

^d Water-resistant formulation of allyl starch (7).

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